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CONCERNING A FILING UNDER 35 U.S.C. § 371**

INTERNATIONAL APPLICATION NO.

PCT/JP99/07312

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TITLE OF INVENTION

METHOD FOR PURIFICATION OF PHOSPHORIC ACID AND HIGH PURITY POLYPHOSPHORIC ACID

APPLICANT(S) FOR DO/EO/US

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application under PCT Article 19 (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information: PCT Request; International Search Report; Notification of Receipt of Record Copy; Notification Concerning Submission or Transmittal of Priority Document; Notice Informing the Applicant of the Communication of the International Application to the Designated Offices; Information Concerning Elected Offices Notified of their Election; return receipt postcard.

CERTIFICATE OF HAND DELIVERY

I hereby certify that this correspondence is being hand filed with the United States Patent and Trademark Office in Washington, D.C. on June 27, 2001

Marieta Luke
Marieta Luke

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| 21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO.....\$1,000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....\$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO.....\$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provision of PCT Article 33(1)-(4)\$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)\$100.00 | | | | CALCULATIONS PTO USE ONLY | |
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| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | | |
| Total claims | 10 - 20 = | 0 | x \$18.00 | \$0.00 | |
| Independent claims | 2 - 3 = | 0 | x \$80.00 | \$0.00 | |
| | | | + \$270.00 | \$0.00 | |
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| <input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. | | | | \$0.00 | |
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**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive
 (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

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SPECIFICATION

**METHOD FOR PURIFICATION OF PHOSPHORIC ACID AND HIGH PURITY
POLYPHOSPHORIC ACID****Technical Field**

5 The present invention relates to a method for purifying
phosphoric acid, which can efficiently reduce the content of
harmful heavy metal, particularly that of arsenic, and to high
purity polyphosphoric acid obtained thereby, which is expected
to be applicable to a broader range of use in the fields of food,
10 medicaments and electronic materials.

Background Art

As a production method of phosphoric acid, there have been
known a wet method and a dry method, and phosphoric acid is
industrially produced by one of these methods. In the wet
15 method, phosphorous ore is dissolved in sulfuric acid, a gypsum
component is filtered off to produce dilute phosphoric acid
having a low concentration, and the dilute phosphoric acid is
concentrated to a desired level to give phosphoric acid. In the
dry method, phosphorous ore is reduced in an electric furnace to
20 give yellow phosphorus, which is burnt to give phosphoric
anhydride, which is then hydrated to give phosphoric acid. In
general, the wet method does not require reduction or combustion
and is considered to be advantageous from the aspect of
production cost. The dry method is considered to be
25 advantageous from the aspect of quality, because the production
via phosphoric anhydride reduces contamination of impurities
derived from phosphorous ore. In any production method, however,
the obtained phosphoric acid contains arsenic derived from
phosphorous ore or phosphoric anhydride, which is harmful for
30 human body, in generally about several dozen ppm, and the
arsenic is removed by a sulfide coagulation method according to
the use of the phosphoric acid. A conventional method for
removing arsenic is applicable only to phosphoric acid having a
 P_2O_5 concentration of up to about 60%.

35 High concentration phosphoric acid, particularly

polyphosphoric acid (P_2O_5 concentration of not less than 72.4%), is also produced by the aforementioned wet method or dry method, like phosphoric acid. Polyphosphoric acid produced by the dry method generally shows lower heavy metal, silica and sodium contents because the production goes through phosphoric anhydride. However, it contains arsenic derived from phosphoric anhydride in about 5-100 ppm, because a conventional method for removing arsenic cannot be applied to high concentration phosphoric acid. Polyphosphoric acid produced by the wet method shows a low arsenic content of less than 1 ppm because a conventional method for removing arsenic can be applied before concentration. On the other hand, it characteristically shows high contents of heavy metal, silica and sodium derived from phosphorous ore. High concentration phosphoric acid, particularly polyphosphoric acid, which characteristically shows a low arsenic content and low contents of heavy metal, silica and sodium, has not been obtained.

When phosphoric acid having a P_2O_5 concentration of up to about 60%, which is obtained by a dry method, is subjected to a dearsenic treatment by a conventional sulfide coagulation method and the like and concentrated, polyphosphoric acid having low contents of arsenic, heavy metal, silica and sodium is presumably obtained. However, such production method has not been put to practical use. This is because equipment for burning and hydrating yellow phosphorus and for highly concentrating the resulting phosphoric acid is required, which is extremely disadvantageous from the economical point of view, due to high facility costs and high operation costs.

The arsenic contained in phosphoric acid and polyphosphoric acid is particularly problematic for a use that requires high purity, in the fields of food, medicaments, electronic materials and the like. Given the high attention to the environmental problems in recent years, moreover, phosphoric acid and polyphosphoric acid having a low arsenic content are desired as industrial phosphoric acid to be used for metal

surface treatment, dye processing and the like. Therefore, a method for removing arsenic, which affords efficient operation at lower costs, is demanded.

Known methods for removing arsenic from phosphoric acid include (1) sulfide coagulation method, (2) solvent extraction method and (3) ion exchange method. Of these, the sulfide coagulation method is most popular because the required steps and equipment are rather simple and this method is operable at a low cost. This method includes bringing phosphoric acid into contact with hydrogen sulfide, or sodium sulfide, sodium hydrosulfide and the like, which produce hydrogen sulfide upon dissolution in phosphoric acid, to allow precipitation of arsenic as arsenic sulfide, which is followed by separation for removal. In contrast, the solvent extraction method and ion exchange method are less popular because of the complicated steps and complicated equipment, as well as higher costs.

However, the sulfide coagulation method, too, requires filtration equipment, such as vacuum filter, press filter, centrifuge separator and the like. The precipitated arsenic sulfide tends to become a gel, which makes it difficult to separate and remove arsenic from phosphoric acid. For facilitated separation, a method (Japanese Unexamined Publication No. 6-48712) comprising passage through an activated carbon tower, and a method (Japanese Unexamined Publication No. 6-100307) comprising addition of a chelating resin are used. These methods are unpreferable because the facility and treatment costs become higher.

When hydrogen sulfide remains in phosphoric acid, moreover, corrosion of phosphoric acid is enhanced, thus necessitating deaeration of excess hydrogen sulfide with air or nitrogen, which in turn makes the step complicated. When compounds such as sodium sulfide, sodium hydrosulfide and the like are used, this method cannot be applied to a use where a sodium content matters, since sodium remains in a large amount in phosphoric acid.

In the case of the sulfide coagulation method, when the phosphoric acid concentration is high, particularly in the case of polyphosphoric acid, phosphoric acid itself comes to have a higher viscosity, thereby making the separation for removal of arsenic sulfide more difficult. Therefore, this method is applicable to phosphoric acid having a P_2O_5 concentration of about 60% at most.

The method for removing arsenic from phosphoric acid having a higher concentration is disclosed in Japanese Examined Publication No. 53-128595 as the purification method of phosphoric acid by a wet method. According to this method, sodium chloride is added to phosphoric acid having a P_2O_5 concentration of up to about 82% to allow reaction of arsenic in phosphoric acid with chlorine for separation and removal. Because this method involves the use of sodium chloride in 1000-2000 ppm, sodium remains in a great amount in phosphoric acid after removing arsenic.

The conventional methods for removing arsenic require a filtration step and a deaeration step, both of which are costly, and sodium remains in a great amount in phosphoric acid. They cannot be applied to high concentration phosphoric acid having a P_2O_5 concentration of not less than 60%, particularly polyphosphoric acid. In addition, there has not been obtained high concentration phosphoric acid, particularly polyphosphoric acid, having lower contents of arsenic, heavy metal, silica and sodium, by a method operable at a low cost. Therefore, the field of use of polyphosphoric acid has been limited to the field free of a high purity requirement.

The present invention provides a completely new method for removing arsenic from phosphoric acid, which is operable at a low cost, which requires no filtration step or deaeration step but is free of a large amount of residual sodium, unlike sulfide coagulation method, and which is applicable to high concentration phosphoric acid, particularly polyphosphoric acid. In addition, the present invention aims at obtaining high

purity polyphosphoric acid having low contents of arsenic, heavy metal, silica and sodium, which has not been conventionally obtained.

Disclosure of the Invention

- 5 The present inventors have conducted intensive studies in an attempt to solve the above-mentioned problems and found that the arsenic content of phosphoric acid drastically falls during an organic synthetic reaction accompanying production of hydrogen chloride in high concentration phosphoric acid.
- 10 Further investigation thereof has revealed that this organic synthetic reaction itself has nothing to do with an arsenic removal effect but, by bringing phosphoric acid into contact with hydrogen halide, the arsenic content of phosphoric acid can be reduced to not more than about 1 ppm, that, when the contact
- 15 is performed in the presence of a compound capable of generating hydrogen halide under acidic conditions, the arsenic removal effect is enhanced, and that this method is useful for removing arsenic particularly from polyphosphoric acid, which resulted in the completion of the present invention.
- 20 Accordingly, the present invention provides the following.
- (1) A method for purifying phosphoric acid, which comprises bringing phosphoric acid containing arsenic into contact with hydrogen halide, thereby to remove the arsenic from the phosphoric acid.
- 25 (2) The purification method of (1) above, wherein the phosphoric acid containing the arsenic is brought into contact with hydrogen halide in the presence of a compound capable of generating hydrogen halide under acidic conditions.
- (3) The purification method of (2) above, wherein the compound
- 30 capable of generating hydrogen halide under acidic conditions is added in a proportion of less than 1 wt% of a weight of the phosphoric acid.
- (4) The purification method of (2) above, wherein the compound capable of generating hydrogen halide under acidic conditions is
- 35 a chloride of iron(II), copper(I) or tin(II).

(5) The purification method of (1) above, wherein the hydrogen halide is hydrogen chloride.

(6) The purification method of (1) above, wherein the phosphoric acid has a P_2O_5 concentration of not less than 72.4%.

5 (7) A high purity polyphosphoric acid having an iron (Fe) content of not more than 20 ppm, a sodium (Na) content of not more than 100 ppm, a silica (SiO_2) content of not more than 50 ppm and an arsenic (As) content of not more than 1 ppm.

(8) The high purity polyphosphoric acid of (7) above, wherein
10 the iron (Fe) content is not more than 10 ppm, the sodium (Na) content is not more than 5 ppm, the silica (SiO_2) content is not more than 5 ppm and the arsenic (As) content is not more than 1 ppm.

(9) The high purity polyphosphoric acid of (7) above, which has
15 a chromium (Cr) content of not more than 5 ppm, a nickel (Ni) content of not more than 5 ppm and a molybdenum (Mo) content of not more than 5 ppm.

(10) The high purity polyphosphoric acid of (8) above, wherein
20 the chromium (Cr) content is not more than 2 ppm, the nickel (Ni) content is not more than 2 ppm and the molybdenum (Mo) content is not more than 2 ppm.

Before explaining the present invention in detail, the indication of the phosphoric acid concentration is explained in the following.

25 In the present invention, phosphoric acid is a polycondensation product of orthophosphoric acid, and its concentration is generally expressed after orthophosphoric acid conversion or P_2O_5 conversion. Phosphoric acid having an orthophosphoric acid concentration of 100% corresponds to
30 phosphoric acid having a P_2O_5 concentration of 72.4%, wherein the relationship between both concentrations is expressed by the following equation:

$$P_2O_5 \text{ concentration (\%)} = \text{orthophosphoric acid concentration (\%)} \times 0.724$$

35 Phosphoric acid having a P_2O_5 concentration of less than

72.4% is an aqueous phosphoric acid solution containing a polycondensation product of orthophosphoric acid and water in an equilibrium state. Phosphoric acid having a P_2O_5 concentration of not less than 72.4% consists solely of a polycondensation product of orthophosphoric acid and is called polyphosphoric acid, strong phosphoric acid or super phosphoric acid. In the present invention, any phosphoric acid concentration is expressed in P_2O_5 concentration.

In a first embodiment of the method for purifying phosphoric acid according to the present invention, phosphoric acid containing arsenic is brought into contact with hydrogen halide alone and the arsenic is removed from the phosphoric acid.

The reason why an arsenic removal effect is expressed by this method is uncertain, but it is postulated that hydrogen halide causes arsenic in phosphoric acid to convert to an arsenic compound having a high volatility, such as arsenic halide and arsenic hydride, and the compound evaporates at a treatment temperature of the purification method of the present invention and is discharged from the system along with hydrogen halide. It is also unknown as to the chemical state of arsenic in phosphoric acid, but the arsenic is considered to be in the state of arsenic acid, arsenious acid, diarsenic pentaoxide, diarsenic trioxide and the like.

While the phosphoric acid concentration applicable to the first embodiment is free of any particular limitation, when the method is applied to low concentration phosphoric acid, hydrogen halide is dissolved in water to enhance corrosion of phosphoric acid and to cause hydrogen halide to remain after treatment. Thus, this method is advantageously applied to phosphoric acid having relatively lower water content (high phosphoric acid concentration). Particularly, when it is applied to polyphosphoric acid, which is completely anhydrous, hydrogen halide does not remain in polyphosphoric acid, thus enabling elimination of corrosion. When the phosphoric acid to be used is polyphosphoric acid, a concentration range free of freezing

point, namely, a P_2O_5 concentration of 75-77% or not less than 80% is preferable. In consideration of handling property, the upper limit of P_2O_5 concentration is preferably 90%.

In a second embodiment of the method for purifying
5 phosphoric acid of the present invention, phosphoric acid containing arsenic is brought into contact with hydrogen halide in the presence of a compound capable of generating hydrogen halide under acidic conditions, and the arsenic is removed from the phosphoric acid. In this embodiment, arsenic can be removed
10 highly efficiently. The compound capable of generating hydrogen halide under acidic conditions may be an organic or inorganic compound. Particularly, it is preferably metal halide having a reducing action, more preferably halide of iron(II), copper(I) or tin(II), most preferably chloride of these metals,
15 particularly preferably chloride of iron(II) or tin(II).

When phosphoric acid containing arsenic is brought into contact with hydrogen halide in the presence of a compound capable of generating hydrogen halide under acidic conditions, the arsenic removal effect is promoted for unknown reasons, but
20 it is postulated that arsenic itself becomes easily reducible and easily becomes a volatile arsenic compound, such as arsenic halide and arsenic hydride, which is easily evaporated at the treatment temperature of the purification method of the present invention, because the effect is particularly striking when
25 metal halide acting as a reducing agent is added.

The compound capable of generating hydrogen halide under acidic conditions in the second embodiment is added in a trace amount, which is preferably less than 1 wt%, more preferably less than 0.5 wt%, of a weight of phosphoric acid. When it is
30 used in a greater amount, an arsenic removal effect is assumed to be enhanced more. Particularly when this compound is metal halide, however, an impurity derived from a metal in the metal halide unpreferably remains. When the residual impurity is to be avoided, or when high purity phosphoric acid, particularly
35 high purity polyphosphoric acid is desired, the first embodiment

wherein phosphoric acid containing arsenic is brought into contact with hydrogen halide alone is preferable rather than the second embodiment.

In the first and the second embodiments, phosphoric acid
5 is brought into contact with hydrogen halide in any typical gas-liquid mixing apparatus, which may be of a batch type or a continuous type. For example, a method wherein a batch reaction vessel is used and phosphoric acid is vigorously stirred with direct blowing of hydrogen halide therein, a method wherein a
10 static mixer or ejector is used and phosphoric acid and hydrogen halide are continuously mixed, a method wherein the both methods are combined, and the like can be employed. The hydrogen halide to be used in the present invention may be hydrogen chloride, hydrogen bromide and the like, with preference given to hydrogen
15 chloride because it is obtained most easily and economically.

In the first and the second embodiments, the necessary amount of hydrogen halide relative to phosphoric acid depends greatly on the gas-liquid mixing efficiency of the apparatus used, and the range of the amount is difficult to specify.
20 Because arsenic in phosphoric acid is considered to be trivalent or pentavalent, at least not less than 3 to 5 molar equivalents of hydrogen halide relative to the arsenic content is considered to be necessary. In the case of the easiest method wherein a batch reaction vessel is used and phosphoric acid is vigorously
25 stirred with direct blowing of hydrogen halide therein, for example, hydrogen chloride is blown into 500 ml of polyphosphoric acid (P_2O_5 concentration 85%) having an arsenic content of 50 ppm preferably at a rate of 1-100 ml/min, more preferably 10-80 ml/min, for preferably not less than 30 min,
30 more preferably not less than 60 min.

In the first and the second embodiments, the treatment temperature varies depending on the phosphoric acid concentration and the material of the reactor, but may be any within the range of from about 50°C to 200°C. In consideration
35 of the corrosion of a stainless material industrially used for a

reactor and the like by phosphoric acid, it is desirably not more than 150°C. For promotion of evaporation of the generated arsenic compound, it is desirably at least 50°C, more preferably not less than 100°C. The pressure is free of any particular
5 limitation and can be set optionally, wherein a sufficient dearsenic effect can be achieved under an atmospheric pressure.

In the first and the second embodiments, moreover, the arsenic compound is discharged from the system together with hydrogen halide. These compounds may be preferably absorbed by
10 water and neutralized, or absorbed by an aqueous alkaline solution of sodium hydroxide, potassium hydroxide and the like.

According to the method for purifying phosphoric acid of the present invention, phosphoric acid having a low arsenic content of not more than about 1 ppm can be obtained by an easy
15 method. Particularly, when the method is applied in the presence of a compound capable of generating hydrogen halide under acidic conditions, phosphoric acid having a low arsenic content of not more than about 0.1 ppm can be obtained.

Inasmuch as the method does not require an equipment cost for a
20 filtration step or a deaeration step or the use of a sodium compound, such as sodium sulfide, sodium hydrosulfide and the like, unlike the conventional method, it does not happen that sodium remains in a large amount in phosphoric acid. By the application of the purification method of the present invention
25 to phosphoric acid having low contents of heavy metal, sodium and silica, which is obtained by the dry method, phosphoric acid having a low arsenic content and low contents of heavy metal, silica and sodium can be obtained.

The method for purifying phosphoric acid of the present
30 invention does not require conventional filtration steps. Therefore, the method is applicable to high concentration phosphoric acid, particularly polyphosphoric acid. By the application of the purification method of the present invention to polyphosphoric acid having low contents of heavy metal,
35 silica and sodium but a high arsenic content, which is obtained

by the dry method, high purity polyphosphoric acid having a low arsenic content and low contents of heavy metal, silica and sodium, which has not been obtained heretofore, can be afforded.

To be specific, by the application of the purification method of the present invention to polyphosphoric acid prepared by adding phosphoric anhydride to industrial phosphoric acid and dissolving therein, polyphosphoric acid having an iron (Fe) content of not more than 20 ppm, a sodium (Na) content of not more than 100 ppm, a silica (SiO_2) content of not more than 50 ppm, and an arsenic (As) content of not more than 1 ppm, and further, a chromium (Cr) content of not more than 5 ppm, a nickel (Ni) content of not more than 5 ppm, and a molybdenum (Mo) content of not more than 5 ppm can be obtained.

By the application of the purification method of the present invention to polyphosphoric acid prepared by adding phosphoric anhydride to phosphoric acid as a reagent or phosphoric acid as a food additive and dissolving therein, polyphosphoric acid having an iron (Fe) content of not more than 10 ppm, a sodium (Na) content of not more than 5 ppm, a silica (SiO_2) content of not more than 5 ppm, and an arsenic (As) content of not more than 1 ppm, and further, a chromium (Cr) content of not more than 2 ppm, a nickel (Ni) content of not more than 2 ppm, and a molybdenum (Mo) content of not more than 2 ppm can be obtained.

The content of each element of the polyphosphoric acid in the present invention was measured by the following methods.

Arsenic was measured according to JIS-K 0102 (1993). Inasmuch as an organic substance is considered to be absent from a polyphosphoric acid sample, an organic substance decomposition step with sulfuric acid/nitric acid as described in the JIS was omitted. Iron, chromium, nickel, molybdenum and silica were quantitatively determined by an inductively coupled plasma (ICP) analysis. The ICP sample solution was prepared by adding hydrochloric acid to polyphosphoric acid to give 1.2 M hydrochloric acid solution. A calibration curve of the

phosphoric acid solution was adjusted to achieve the same concentration as the sample solution. Sodium was quantitatively determined by atomic absorption spectrometry. The atomic absorption sample solution was the same as it was for ICP. The
5 P_2O_5 concentration of polyphosphoric acid was determined by titration using 1 M sodium hydroxide solution.

The present invention is explained in more detail in the following by referring to Examples. The present invention is not limited by these examples.

10 Example 1

Commercially available polyphosphoric acid obtained by a dry method (500 ml, P_2O_5 concentration 84.9%) having an arsenic content of 58 ppm was stirred with heating at 130°C, during which a glass tube having a glass bowl filter was inserted and
15 hydrogen chloride gas was blown in at an aeration rate of 20 ml/min for about 2 hours to give high purity polyphosphoric acid. The discharged hydrogen chloride gas was trapped in an aqueous sodium hydroxide solution. The analysis results of the obtained high purity polyphosphoric acid are shown in Table 1.

20 Example 2

Commercially available polyphosphoric acid obtained by a dry method (500 ml, P_2O_5 concentration 84.2%) having an arsenic content of 8 ppm was cast in a 1(one) liter three-necked glass flask and stirred with heating at 150°C, during which a glass
25 tube having a glass bowl filter was inserted and hydrogen chloride gas was blown in at an aeration rate of 50 ml/min for about 2 hours to give high purity polyphosphoric acid. The discharged hydrogen chloride gas was trapped in an aqueous sodium hydroxide solution. The analysis results of the obtained
30 high purity polyphosphoric acid are shown in Table 1.

Example 3

Phosphoric anhydride (200 g) having an arsenic content of 25 ppm was added to phosphoric acid as a reagent (422 g, P_2O_5 concentration 61.5%) having an arsenic content of 0.1 ppm. The
35 mixture was stirred with heating at 120°C to give a homogeneous

liquid, whereby polyphosphoric acid (P_2O_5 concentration 84.0%) having an arsenic content of 8 ppm was prepared. While stirring under heating at $150^{\circ}C$, a glass tube with a glass bowl filter was inserted and hydrogen chloride gas was blown in at an
5 aeration rate of 20 ml/min for about 3 hours to give high purity polyphosphoric acid. The discharged hydrogen chloride gas was trapped in an aqueous sodium hydroxide solution. The analysis results of the obtained high purity polyphosphoric acid are shown in Table 1.

10 Example 4

Phosphoric anhydride (170 g) having an arsenic content of 25 ppm was added to commercially available polyphosphoric acid obtained by a dry method (330 g, P_2O_5 concentration 76.0%) having an arsenic content of 5 ppm. The mixture was stirred
15 under heating at $120^{\circ}C$ to give a homogeneous liquid, whereby polyphosphoric acid (P_2O_5 concentration 84.2%) having an arsenic content of 11 ppm was prepared. While stirring under heating at $150^{\circ}C$, a glass tube with a glass bowl filter was inserted and hydrogen chloride gas was blown in at an aeration rate of 20
20 ml/min for about 3 hours to give high purity polyphosphoric acid. The discharged hydrogen chloride gas was trapped in an aqueous sodium hydroxide solution. The analysis results of the obtained high purity polyphosphoric acid are shown in Table 1.

Example 5

25 Industrial phosphoric acid (500 ml, P_2O_5 concentration 65%) having an arsenic content of 15 ppm was cast in a 1(one) liter three-necked glass flask and stirred with heating at $130^{\circ}C$, during which a glass tube having a glass bowl filter was inserted and hydrogen chloride gas was blown in at an aeration
30 rate of 50 ml/min. The discharged hydrogen chloride gas was trapped in an aqueous sodium hydroxide solution. As a result, the concentration of arsenic in phosphoric acid at 180 minutes after the start of blowing was 0.8 ppm.

Example 6

35 The same treatment as in Example 5 was applied except

that iron chloride(II) (0.1 g) was added before blowing in hydrogen chloride. As a result, the concentration of arsenic in phosphoric acid at 120 minutes after the start of blowing was 0.07 ppm.

5 Example 7

The same treatment as in Example 5 was applied except that tin chloride(II) dihydrate (0.5 g) was added before blowing in hydrogen chloride. As a result, the concentration of arsenic in phosphoric acid at 120 minutes after the start of blowing was
10 0.08 ppm.

The analysis results of each element contained in the high purity polyphosphoric acids obtained in Examples 1-4 are shown in Table 1. For comparison, the analysis results of commercially available product A, which is polyphosphoric acid
15 obtained by a dry method, and commercially available product B, which is polyphosphoric acid obtained by a wet method, are also shown in Table 1.

Table 1

| Analysis item | Example 1 | Example 2 | Example 3 | Example 4 | Commer- cially available product A | Commer- cially available product B |
|---|-----------|-----------|-----------|-----------|---|---|
| P ₂ O ₅ con- centra- tion (%) | 84.9 | 84.2 | 84.0 | 84.2 | 85.0 | 84.3 |
| Fe content | 1.6 | 1.0 | 0.2 | 1.2 | 1.6 | 37 |
| Cr content | 0.8 | 0.1 | 0.1 | 0.7 | 0.8 | 6.3 |
| Ni content | 0.6 | 0.3 | 0.1 | 0.4 | 0.6 | 4.4 |
| Mo content | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | 12 |
| Na content | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 250 |
| SiO ₂ content | <5 | <5 | <5 | <5 | <5 | 120 |
| As content | 0.5 | 0.08 | 0.03 | 0.03 | 58 | 0.02 |

20 In Table 1, respective contents are in the unit of ppm.

As is evident from Table 1, the commercially available product A (polyphosphoric acid obtained by a dry method) showed low contents of heavy metal, silica and sodium but a high
5 arsenic content, and the commercially available product B (polyphosphoric acid obtained by a wet method) showed a low arsenic content but high contents of heavy metal, sodium and silica. In contrast, the high purity polyphosphoric acids of Examples 1-4 showed low arsenic contents, and low contents of
10 heavy metal, sodium and silica. From Examples 6 and 7, it is evident that, when phosphoric acid containing arsenic is brought into contact with hydrogen halide in the presence of a compound capable of generating hydrogen halide under acidic conditions, such as iron chloride(II), tin chloride(II) and the like, an
15 effect of removing arsenic in phosphoric acid can be enhanced.

As is evident from the following explanation, the method for purifying phosphoric acid of the present invention can effectively remove arsenic in phosphoric acid, which is harmful for human being, by a simple manipulation wherein phosphoric
20 acid is brought into contact with hydrogen halide. To be specific, the arsenic content of several dozen ppm of general industrial phosphoric acid can be reduced to not more than about 1 ppm. When the above-mentioned step is applied in the presence of a compound capable of generating hydrogen halide under acidic
25 conditions, the removal to the level of not more than about 0.1 ppm is possible.

This method includes a simple treatment step and requires no special apparatus. As a result, the total cost for the treatment is low, and since a sodium compound is not used,
30 unlike the conventional method, sodium does not remain in a large amount in phosphoric acid.

Moreover, since the method for purifying phosphoric acid of the present invention does not require a filtration step, unlike a conventional purification method, it can be applied to
35 high concentration phosphoric acid, particularly polyphosphoric

acid. Particularly, when polyphosphoric acid obtained by a dry method and having low contents of heavy metal, sodium and silica but a high arsenic content is subjected to the purification method of the present invention, high purity polyphosphoric acid
5 having a low arsenic content and low contents of heavy metal, silica and sodium can be afforded, which has not been obtained heretofore. Such high purity polyphosphoric acid is highly safe and can reduce the environmental burden. Therefore, it is applicable to a broader range of use in the fields of food,
10 medicaments and electronic materials.

This application is based on patent application Nos. 373696/1998 and 230628/1999 filed in Japan, the contents of which are hereby incorporated by reference.

WHAT IS CLAIMED IS

1. A method for purifying phosphoric acid, which comprises bringing phosphoric acid containing arsenic into contact with hydrogen halide, thereby to remove the arsenic from the phosphoric acid.
2. The purification method of claim 1, wherein the phosphoric acid containing the arsenic is brought into contact with hydrogen halide in the presence of a compound capable of generating hydrogen halide under acidic conditions.
3. The purification method of claim 2, wherein the compound capable of generating hydrogen halide under acidic conditions is added in a proportion of less than 1 wt% of a weight of the phosphoric acid.
4. The purification method of claim 2, wherein the compound capable of generating hydrogen halide under acidic conditions is a chloride of iron(II), copper(I) or tin(II).
5. The purification method of claim 1, wherein the hydrogen halide is hydrogen chloride.
6. The purification method of claim 1, wherein the phosphoric acid has a P_2O_5 concentration of not less than 72.4%.
7. A high purity polyphosphoric acid having an iron (Fe) content of not more than 20 ppm, a sodium (Na) content of not more than 100 ppm, a silica (SiO_2) content of not more than 50 ppm and an arsenic (As) content of not more than 1 ppm.
8. The high purity polyphosphoric acid of claim 7, wherein the iron (Fe) content is not more than 10 ppm, the sodium (Na) content is not more than 5 ppm, the silica (SiO_2) content is not more than 5 ppm and the arsenic (As) content is not more than 1

ppm.

9. The high purity polyphosphoric acid of claim 7, which has a chromium (Cr) content of not more than 5 ppm, a nickel (Ni)
5 content of not more than 5 ppm and a molybdenum (Mo) content of not more than 5 ppm.

10. The high purity polyphosphoric acid of claim 8, wherein the chromium (Cr) content is not more than 2 ppm, the nickel (Ni)
10 content is not more than 2 ppm and the molybdenum (Mo) content is not more than 2 ppm.

**COMBINED DECLARATION AND POWER OF ATTORNEY
FOR UTILITY PATENT APPLICATION**

AS A BELOW-NAMED INVENTOR, I HEREBY DECLARE THAT:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR PURIFICATION OF PHOSPHORIC ACID
AND HIGH PURITY POLYPHOSPHORIC ACID

, the specification of which is attached hereto unless the following box is checked:

- ☒ was filed on June 28, 2001 as United States Application Serial No.
or PCT International Application No. 09/869,379 and was amended on
(if applicable).

I HEREBY STATE THAT I HAVE REVIEWED AND UNDERSTAND THE
CONTENTS OF THE ABOVE-IDENTIFIED SPECIFICATION, INCLUDING THE CLAIMS,
AS AMENDED BY ANY AMENDMENT REFERRED TO ABOVE.

I acknowledge the duty to disclose information which is material to the patentability as
defined in 37 C.F.R. § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any
foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International
application which designated at least one country other than the United States listed below and
have also identified below, by checking the box, any foreign application for patent or inventor's
certificate, or PCT International application having a filing date before that of the application on
which priority is claimed:

| Application No. | Country | Date of Filing (day/month/year) | Priority Claimed? |
|-----------------|---------|------------------------------------|---|
| 373696/1998 | Japan | 28/12/1998 | <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No |
| Application No. | Country | Date of Filing (day/month/year) | Priority Claimed? |
| 230628/1999 | Japan | 17/08/1999 | <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No |
| Application No. | Country | Date of Filing (day/month/year) | Priority Claimed? |
| | | | <input type="checkbox"/> Yes <input type="checkbox"/> No |
| Application No. | Country | Date of Filing (day/month/year) | Priority Claimed? |
| | | | <input type="checkbox"/> Yes <input type="checkbox"/> No |

I hereby claim benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below:

| Application Serial No. | Filing Date |
|------------------------|-------------|
| | |

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(e) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

| Application Serial No. | Filing Date | Status |
|------------------------|-------------|---|
| | | <input type="checkbox"/> Patented <input type="checkbox"/> Pending <input type="checkbox"/> Abandoned |

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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